Processing Reliability for Solid Oxide Fuel Cells

July 22-23, 2004

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The reliability of ceramics used for SOFCs depend on the

1) the phase stability of the different materials bonded to one another,
2) their differential properties that gives rise to stresses
3) the processing method used to minimize flaws that reduce strength and dielectric breakdown
4) their microstructure stability, namely, density, pore size and grain size
5) their reaction with the combustion product, water vapor, causing mechanical instability
6) design features that minimize stresses inherent with multiple material, layered systems

These issues will be systematically and sequentially addressed, at the engineering level, with the topics outlined below.

Outline

I. Processing for Reliability

Heterogeneities (organic and inorganic inclusions, and agglomerates) in powders produce flaws that severely reduce strength and induce dielectric breakdown of a ceramic. Colloidal processing of ceramic powders is used to reduce the size of inhomogeneities by filtering dispersed slurries prior to forming an engineering shape. When the idea of removing strength limiting flaws from powders was applied to an industrial process, it was showed that densie bodies could be made stronger, but also, and more importantly, their statistical strenght distribution was truncated. Previously, truncated strength distributions were only observed for a series of proof tested components. It is now obvious that eliminating flaws greater than a given size, determined by the filter through which the slurry is passed, effectively 'proof tests' the powder prior to consolidation and shape forming.

Colloidal processing starts with a slurry, i.e., a mixture of powder and water. A very small fraction of a special chemical is added to the slurry to make the particles repulsive. Understanding how to control and manipulate the forces between particles and how these forces control the slurry rheology and particle packing will be the theme of this section, and will include the following topics:

Flaw populations, how to find them, and their relation to powder processing
Electrostatic and steric methods for controlling forces between particles
Relation between interparticle forces, slurry rheology and particle packing
Forming shapes with slurries, current and future
Application to $Zr(Y)O_2$, LMO, ZrO_2/Ni systems

II Heat Treatment of the Powder

The anode and cathode materials that sandwich the solid-state electrolyte, and, in some designs, the interconnect material, must be heat treated to produce either a fully dense body (the case for the electrolyte) or a strong, put porous material (case for the electrodes) that will not become fully dense. In most designs, all of the different materials are bonded together in the powder state and heat treated at the same time to developed the required microstructure features (density, pore size, grain size, phase connectivity). During heating, although all of the materials shrink to some degree, only the electrolyte needs to become fully dense. Differential shrinkage is a common problem to the fabrication of all SOFCs, causing one material to constrain the shrinkage of its bonded neighbor(s). Constrained shrinkage gives rise flaws, and problems including shape retention and mechanics reliability. Topics required to understand this phenomenon include:

Thermodynamics of densification
Constrained densification in laminar systems
Stabilizing grain size, pore fraction and pore size
Application to $Zr(Y)O_2$, LMO, ZrO_2/Ni, and glass ceramics

III Crack Extension in Brittle Materials

The strength of a ceramic depends on both the flaw size that initiates fracture and the material's resistance to crack extension. For many ceramic applications, such as SOFCs, the largest stress is not those applied by external agents, but stresses that arise due to differential properties of the different materials that form the structure. Although failure is generally though as a catastrophic event (that is, happens rapidly), many materials exhibit sub-critical crack growth where crack extension occurs progressively until a catastrophic event. This, understanding crack extension requires understanding both the catastrophic event and the sub-critical growth phenomena. Here, relations between flaw size, stress and fracture will be summarized for engineers who process SOFCs.

Background for stress, stain, their relation
Background to crack instability (fracture)
Understanding and predicting failure under conditions of sub-critical crack growth

IV Fracture Phenomena Applied to SOFC

Because SOFC systems are formed by layering and bonding different materials, stresses unique to layered systems arise due to differential thermal-elastic properties. Some layers will contain biaxial compresses stress, while other must contain biaxial tensile stresses. In addition, the stresses at surfaces and edges where the layers terminate are much different that the stresses deep within the different layers. These stresses, special to layer systems, produce their own failure problems. In addition, the extension of cracks from one layer to another depend on the residual stresses within each layer, and the volume fraction of the porosity. In addition, the stresses at the edges of the layers produce very special crack extension phenomena important to reliable design.

Residual stresses within layered structures; internal and surface
Crack extension and failure in layered structures
Crack extension in porous ceramics

V Chemical Degradation Phenomena

Water, the product of combustion, reacts with several of the materials used in SOFCs. For example, the yttrium in solid-solution with zirconia is know to form a hydroxide at the surface; this reaction appears to be most rapid at 250 °C. For some rare-earth zirconia materials, the decrease in yttrium at the surface can cause a phase transformation that eventially cause catastrophic failure. Glasses and glass ceramics are commonly used for sealing SOFC stacks. Water reacts with the glass at crack tips to produce a phenomena know as subcritical crack growth. Sub-critical crack growth leads to time dependent failure at low stresses. Lastly, silica (in glass and glass ceramics) reacts with water vapor to form soluble silica hydroxide species that condense in cooler regions. This phenomena not only 'spreads' the silica around the whole system, but also leads to the recession and failure of the glass ceramic itself. The topics in this area include:

Destabilization of $Zr(Y)O_2$ by water
Time dependent failure in glass & glass ceramics
Reaction of silicates with water

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Schedule

Thursday, July 22, 2004

8:30-09:50	Lecture 1
09:50-10:05	Coffee break
10:05-1l:25	Lecture 2
11::25-12:05	First Discussion Period
12:05-13:15	Lunch
13:15-14:35	Lecture 3
14:35-14:50	Coffee break
14:50-16:10	Lecture 4
16:10-16:40	Second Discussion Period

Friday, July 23, 2004

8:30-09:50	Lecture 5
09:50-10:05	Coffee break
10:05-1l:25	Lecture 6
11::25-12:05	Third Discussion Period
12:05-13:15	Lunch
13:15-14:35	Lecture 7
14:35-14:50	Coffee break
14:50-16:10	Lecture 8
16:10-16:40	Forth Discussion Period